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Synthesis of Derivatives of alpha, omega
Difunctional Perfluoroaliphatic Compounds for Low Dielectric
Constant Resins

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<p>Copper coupling reactions of perfluoroalkyl iodides with certain aryl iodides have been studied. Simple trial tests were carried out between perfluorooctyl iodide and iodobenzene and between perfluorohexyl iodide and 4-iodophenol. The desired products were obtained in good yield. However, the coupling of 1,6-diiodoperfluorohexane and 4-iodophenol gave a product which could not be isolated or purified. Protection of the phenolic OH by methylation or acetylation gave the coupled alpha, omega products in good yield.</p>					
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Synthesis of Derivatives of alpha, omega
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Constant Resins

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The final report of our investigations of the synthesis of key intermediates in the preparation of cyanate resins is included below.

The object of this study was to examine variables in the copper coupling reaction of iodophenols and iodophenol derivatives with alpha, omega diiodoperfluoroalkanes. Among the variables examined were length of the perfluorocarbon chain and functional derivatives of the phenolic hydroxyl such as methyl ethers and acetates.

Other variables in the study included variations in reactant molar ratios, reaction temperature, reaction time and solvents. The principal problems encountered in the synthesis procedures was the inherent instability in the para coupled fluoroalkylphenols. All indications of the reaction conditions led us to conclude that the desired coupling had taken place but isolation or purification of the bis (4-hydropyphenyl) perfluoroalkanes was never achieved.

Protection or conversion of the phenolic hydroxyl to the methyl ether enabled us to prepare in high yield the desired alpha, omega bis (4 methoxyphenyl)perfluoroalkanes. Subsequent conversion of these methyl ethers to the free phenol by boron tribromide and further reaction without purification to the cyanates were carried out at the Navy Research Laboratory, Washington, D.C. by Dr. Arthur Snow.

Experimental

The perfluoroalkyl iodides, aromatic iodides, and copper powder used were obtained commercially and were not purified with the exception of iodobenzene and p-iodophenol, which were prepared by previously reported methods. The DMSO was dried over CaH₂ and distilled under vacuum. Measurements and associated instruments are: infrared spectra, Perkin-Elmer Model 1320; ¹H and ¹⁹F NMR, Varian Model EM-360L using TMS and CFC1₃ as internal standards; mass spectra, Varian Saturn Model GC/MS. All melting points are uncorrected. The first reaction is given in complete detail. All of the other work-ups were the same. In some cases the procedure was altered, but the changes are noted.

1-(4'-hydroxyphenyl)perfluorohexane. A mixture of 6.61 g (30 mmol) of 3-iodophenol, 8.93 g (20 mmol) of 1-iodoperfluorohexane, 6.35 g (100 mmol) copper powder, and 7.5 g DMSO was placed in a 100 mL round-bottomed flask in a N₂ dry box, fitted with a reflux condenser and N₂ inlet, and heated (under N₂) in an oil bath at 140°C for 15 hours. The

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mixture was poured into a 1000 mL beaker containing 300 mL H₂O and 25 mL conc. HCl and stirred rapidly for 45 min. The H₂O was decanted, and another 300 of H₂O was added followed by 1 hour of stirring. The mixture was then vacuum filtered, and the copper layer was washed with 100 mL of ether. The solids were dried and weighed 12.1 g, and the organic liquid was washed three times with 50 mL saturated aqueous NaCl solution. The organic layer was drained into a 250 Erlenmeyer flask with MgSO₄. After evaporating most of the ether, the crude product was sublimed in 0.05-0.15 mm Hg and 60°C for 12 hours, and yellow crystals were recovered and recrystallized with a minimum of methanol. The product was dried and weighed 2.0 g (24% yield); mp 48.5-50.5 C; ¹H Nmr (CDCl₃) 5.18 ppm s (1H), 6.90 ppm d (2H); MS 412 (12.0%) product, 393 (19.9%) product-1F, and 143 (100%) CF₂C₆H₄OH.

1-Phenyl-perfluorooctane. Using a similar reaction procedure above, then after evaporating the ether, the crude product was distilled under 30 mm Hg, and 1.7 g of product was recovered at 90-120°C (28% yield): ¹H NMR -(CDCl₃) 7.26 ppm s (1H, CHCl₃) and 7.63 ppm m (5H); ¹⁹F NMR (CDCl₃) -80.4 ppm t (CF₃), -109.3 ppm t (CF₂-Ph), -120.0 ppm m (-CF₂-), and 124.8 ppm m (CF₂-CF₃); IR (KBr) aromatic C-H stretch (307cm⁻¹), C-H ring stretch (1610 and 1460), CF₂ and CF₃ stretch (1270-1130), and out-of plane ring C-H bend (700).

1-(4'-hydroxyphenyl)perfluorooctane. Preparation was carried out similar to the above reaction. The product appeared as 9.2 g of white crystals (71.9% yield): mp 72-72°C; ¹H NMR (CDCl₃) 5.68 ppm s (1H), 6.75 ppm q (2H), and 7.45 ppm q (2H); ¹⁹F NMR (CDCl₃) -80.5 ppm t (CF₃), -108.3 ppm t (CF₂-Ph), -120.7 ppm m (-CF₂-) and -124.4 ppm m (CF₂-CF₃); IR (KBr) OH stretch (3600-3200), aromatic C-H stretch (3070), C-C ring stretch (1615 and 1450), CF₂ and CF₃ stretch (1280-1100), and out-of-plane ring C-H bend (680).

1,6-Bis(4' acetophenyl)perfluorohexane. The crude product (tan crystals) was placed in 250 mL round-bottomed flask with 1.0 g NaOAc and 30 mL acetic anhydride and refluxed for 1 hour. The mixture was then poured into a 500 mL beaker with 100 mL H₂O stirred for 5 hours, and vacuum filtered. After 6 days of drying, 4.5 g of product as white crystals (65.8% yield): mp 199-121°C; ¹H NMR (CDCl₃) 2.30 ppm s (6H), 7.18 q (4H), and 7.55 ppm q (4H); ¹⁹F NMR (CDCl₃) -113.0 ppm t (-CF₂-Ph) and -124.4 ppm m (CF₂-CF₃); IR (KBr) aromatic C-H stretch (3060), CH₃ stretch (2940), C=O stretch (1750), C-H ring stretch (1610 and 1510), and CF₂ and CF₃ stretch (1250-1170); MS no molecular ion, 186 (100%) CF₂C₆H₄O₂CCH₃.

1.4 Bis (4'-methoxyphenyl)perfluorobutane. The product appeared as 1.1 g of white crystals (13.3% yield): mp 47.6-49.1°C; ¹H MNR (CDCl₃) 3.75 ppm s (6H), 6.80 ppm d (4H), and 7.55 ppm d (4H); IR (KBr) aromatic C-H stretch (3020), CH₃ stretch (2980 and 2860), C-C ring stretch (1600 and 1500), asymmetric C-O-C stretch (1260), and CF₂ stretch (1190).

1-(4'-methoxyphenyl)perfluorooctane. The product was sublimed, and 5.4 g of white crystals were collected (51.3% yield): mp 31-32°C; ^1H NMR (CDCl_3) 3.80 ppm s (3H) and 7.25 ppm (5H); IR (KBr) aromatic C-H stretch (3020), CH_3 stretch (2970 and 2940), C-C ring stretch (1620 and 1530), CF_2 and CF_3 stretch (1310-1200), and out-of-plane ring C-H bend (670); MS 526 (40.0%) product, 507 (15.0%) product -1F, and 157 (100%) $\text{CF}_2\text{C}_6\text{H}_4\text{OCH}_3$.

1-(4'-hydroxyphenyl)perfluorohexane. The product appeared as 2.0 g of yellow crystals (24% yield): mp 48.5-50.5°C; ^1H NMR (CDCl_3) 5.18 ppm s (1H), 6.90 ppm d (2H), and 7.50 ppm d (2H); IR (KBr) OH stretch (3550-3200), C-C ring stretch (1620, 1540, and 1470), CF_2 and CF_3 stretch (1310-1190, and out-of plane ring C-H bend (650); MS 412 (12.0%) product, 393 (19.9%) product-1F, and 143 (100%) $\text{CF}_2\text{C}_6\text{H}_4\text{OH}$.

1-(3'-methoxyphenyl)perfluorooctane. After evaporating the ether, the mixture was distilled, and 6.1 g of product was recovered at 216-235°C (58% yield): ^1H NMR (CDCl_3) 3.70 ppm s (3H) and 7.18 ppm m (4H); MS 526 (93.48%) product, 507 (3.75%) product-1F, 157 (100%) $\text{CF}_2\text{C}_6\text{H}_4\text{OCH}_3$.

1,4-Bis[3'5'-bis(2-hydroxyhexafluoro-2-propyl)phenyl]-perfluorobutane. The product appeared as 3.1 g of yellow crystals (30.5% yield): mp 126-128°C; ^1H NMR (CDCl_3) 3.40 ppm d (4H), 7.24 ppm s (1H, CHCl_3), 7.78 ppm s (2H), 8.05 ppm s (2H), and 8.31 ppm s (2H); IR (KBr) OH stretch (3660-3590), aromatic C-H stretch (3140), C-C ring stretch (1590), CF_2 and CF_3 stretch (1270-1170), and C-O stretch (1010); MS molecular ion not present, 459 (100%) $\text{CF}_2\text{C}_6\text{H}_3(\text{C}_3\text{F}_6\text{OH})_2$.

1,6-Bis[3'5'-bis(2-hydroxyhexafluoro-2-propyl)phenyl]-perfluorohexane. The product appeared as 4.3 g of yellow crystals (48% yield): mp 94-98°C; MS molecular ion not present, 459 (100%) $\text{CF}_2\text{C}_6\text{H}_3(\text{C}_3\text{F}_6\text{OH})_2$.

1-(3'-hydroxyphenyl)perfluorooctane. The product appeared as 3.4 g of tan crystals (22% yield): mp 36-69 C; MS 512 (42%) product, 493 (7%) product-1F, 143 (100%) $\text{CF}_2\text{C}_6\text{H}_4\text{OH}$.

1,6-Bis[3'5'-bis(2-hydroxyhexafluoro-2-propyl)phenyl]-perfluorohexane. The product appeared as 4.3 g of yellow crystals (58.6% yield); IR (KBr) OH stretch (3600-3200), aromatic C-H stretch (3150), CF_2 and CF_3 stretch (1320 - 1200), and C-O stretch (1010); MS no molecular ion present, 459 (100%) $\text{CF}_2\text{C}_6\text{H}_3(\text{C}_3\text{F}_6\text{OH})_2$.